FORM PTO-1390 (Modified) (REV 10-95) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	
2075	
U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	
10/088620	

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/DE 00/03135	SEPTEMBER 9, 2000	SEPTEMBER 21, 1999

TITLE OF INVENTION

METHOD FOR MOUNTING FLAT EXTERNAL ELECTRODES ON A PIEZOELECTRIC MULTI-LAYER ACTUATOR

APPLICANT(S) FOR DO/EO/US

Wilfried RESCHNAR, Lothar HENNEKEN, Bertram SUGG, Juergen HACKENBERG

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ A copy of the International Search Report (PCT/ISA/210).
8. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
    A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☒ Certificate of Mailing by Express Mail
19. ☐ Other items or information:

EL 796689274 US

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/088620	PCT/DE 00/03135	2075

20. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS PTO USE ONLY
☐	Search Report has been prepared by the EPO or JPO	**$930.00**
☐	International preliminary examination fee paid to USPTO (37 CFR 1.482)	**$720.00**
☐	No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	**$790.00**
☒	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO	**$1,070.00**
☐	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	**$98.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =	**$890.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$0.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	24 - 20 =	4	x $18.00	**$72.00**	
Independent claims	1 - 3 =	0	x $80.00	**$0.00**	
Multiple Dependent Claims **(check if applicable).**			☐	**$0.00**	
TOTAL OF ABOVE CALCULATIONS =				**$962.00**	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) **(check if applicable).** ☐				**$0.00**	
SUBTOTAL =				**$962.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				**$0.00**	
TOTAL NATIONAL FEE =				**$962.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐				**$0.00**	
TOTAL FEES ENCLOSED =				**$962.00**	
				Amount to be: refunded	$
				charged	$

☐ A check in the amount of to cover the above fees is enclosed.

☒ Please charge my Deposit Account No. **19-4675** in the amount of **$962.00** to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **19-4675** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

STRIKER, STRIKER & STENBY
103 EAST NECK ROAD
HUNTINGTON, NEW YORK 11743

SIGNATURE

MICHAEL J. STRIKER
NAME

27233
REGISTRATION NUMBER

MARCH 19, 2002
DATE

UNITED STATES PATENT AND TRADEMARK OFFICE

Examiner: Group: Attorney Docket # 2075

Applicant(s) : RESCHNAR, W.,E T AL

Serial No. :

Filed :

For : METHOD FOR MOUNTING FLAT EXTERNAL ELECTRODES ON A PIEZOELECTRIC MULTI-LAYER ACTUATOR

SIMULTANEOUS AMENDMENT

March 19, 2002

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

S I R S:

Simultaneously with filing of the above identified application please amend the same as follows:

In the Claims:

Cancel all claims without prejudice.

Substitute the claims attached hereto.

REMARKS:

This Amendment is submitted simultaneously with filing of the above identified application.

With the present Amendment applicant has amended the claims so as to eliminate their multiple dependency.

Consideration and allowance of the present application is most respectfully requested.

Respectfully submitted,

Michael J. Striker
Attorney for Applicant(s)
Reg. No. 27233

Claims

1. A method for mounting flat external electrodes (15, 16) on a piezoceramic multi-layer actuator (10), by which the internal electrodes (12), extended in alternation outward toward opposed outer sides, are each connected parallel, characterized by the treatment of at least the outer faces that are to be provided with the external electrodes (15, 16) by the following method steps:

a) fine cleaning with a neutral cleaning agent;

b) pickling in a dilute acid solution;

c) activation in a dilute solution of an activation agent;

d) germination in a dilute solution of palladium chloride with an addition of halide ions or of another halide of a metal of the platinum group with palladium or another metal of the platinum group;

e) currentless deposition of nickel and/or copper by means of a reducing agent in a suitable nickel salt and/or copper salt solution;

f) electrolytic deposition of tin or a tin alloy in a suitable solution;

g) drying and/or tempering;

h) exerting superficial pressure on the flexible external

electrodes (15, 16) to which solder has already been applied; and

i) applying solder to the external electrodes (15, 16) in protective gas.

2. The method of claim 1, characterized in that the fine cleaning is done with a neutral cleaner, having a pH value of 68, at a temperature preferably of 40 to 60°C.

3. The method of claim 1 [or 2], characterized in that the pickling is done in a dilute solution of nitric acid with acid additives.

4. The method of [one of the foregoing claims] claim 1, characterized in that the pickling is done with ultrasonic support, in particular at a frequency of over 40 kHz and at a temperature of 20 to 30°C.

5. The method of [one of the foregoing claims] claim 1, characterized in that the activation is done in a dilute solution of tin (II) tetrafluoroborate ($Sn(BF_4)_2$) or stannous chloride ($SnCl_2$).

6. The method of [one of the foregoing claims] claim 1, characterized in that the activation is done at a slightly acidic pH value and/or at a temperature of 30 to 40°C.

7. The method of [one of the foregoing claims] claim 1, characterized in that the germination is done in a dilute solution of palladium chloride with an addition of halide ions at a pH value of 3 to 4, and in particular at a temperature of 20 to 30°C.

8. The method of [one of the foregoing claims] claim 1, characterized in that in the currentless deposition, nickel is precipitated out from a nickel salt solution (such as $NiSO_4$), with phosphinates (such as NaH_2PO_2) as a reducing agent.

9. The method of claim 8, characterized in that the deposition is done at a pH value of 8 to 9 and/or at a temperature of 70 to 95°C.

10. The method of [one of claims 1-7] claim 1, characterized in that in the currentless deposition, nickel and copper are precipitated out of a nickel salt solution (such as $NiSO_4$) and a copper salt solution (such as $CuSO_4$) with phosphinates (such as NaH_2PO_2) as the reducing agent and with a hydroxycarboxylic acid as the complexing agent.

11. The method of [one of claims 1-7] claim 1, characterized in that in the currentless deposition, copper is precipitated out of a copper salt solution (such as $CuSO_4$) with formaldehyde (CH_2O) as the reducing agent and with a polyaminopolycarboxylic acid as the complexing agent.

12. The method of claim 10 [or 11], characterized in that the deposition is done at a pH value of 9 to 10 and/or at a temperature of over 60°C.

13. The method of [one of claims 8-11] claim 8, characterized in that the deposition is performed over a period of time of 10 to 20 minutes.

14. The method of [one of the foregoing claims] claim 1, characterized in that in the electrolytic deposition of tin or

tin alloys, organic additives, in particular polyaminopolycarboxylic acid, are used as complexing agents.

15. The method of claim 14, characterized in that the deposition is done at a slightly acidic pH value and/or at a temperature of 20 to 40°C.

16. The method of claim 14 [or 15], characterized in that the deposition is performed over a period of 5 to 30 minutes at a current of 1 to 2 A/dm².

17. The method of [one of the foregoing claims] claim 1, characterized in that the drying is done in the oil-free nitrogen gas stream.

18. The method of [one of the foregoing claims] claim 1, characterized in that the tempering is done in a forced air oven at 100 to 200°C over a period of 30 to 60 minutes.

19. The method of [one of the foregoing claims] claim 1, characterized in that before the exertion of superficial pressure on the external electrodes (15, 16), an ensuing washing off of unneeded flux (no-clean flux) is applied to the suitable outer faces of the multi-layer actuator (10), in particular a 2% adipic acid in ethanol.

20. The method of [one of the foregoing claims] claim 1, characterized in that for the application of solder, the external electrodes (15, 16) are pressed flat onto the surface mounting metallizing with a pressure of 1 to 5 N/mm².

21. The method of [one of the foregoing claims] claim 1,

characterized in that the application of solder to the external electrodes (13, 14) is done in a continuous furnace at a temperature of 250 to 400°C, and in particular at a feeding speed of 300 to 600 mm/min.

22. The method of [one of claims 1-20] claim 1, characterized in that the application of solder to the external electrodes (13, 14) is done in a vapor-phase soldering system at a temperature of 250 to 290°C.

23. The method of [one of the foregoing claims] claim 1, characterized in that the activation and/or germination of the desired faces is done by ram application.

24. The method of claim 23, characterized in that the activation and/or germination is done by ram pressure over a period of time of 0.5 to 2 minutes each, in particular at room temperature.

Claims

1. A method for mounting flat external electrodes (15, 16) on a piezoceramic multi-layer actuator (10), by which the internal electrodes (12), extended in alternation outward toward opposed outer sides, are each connected parallel, characterized by the treatment of at least the outer faces that are to be provided with the external electrodes (15, 16) by the following method steps:

a) fine cleaning with a neutral cleaning agent;

b) pickling in a dilute acid solution;

c) activation in a dilute solution of an activation agent;

d) germination in a dilute solution of palladium chloride with an addition of halide ions or of another halide of a metal of the platinum group with palladium or another metal of the platinum group;

e) currentless deposition of nickel and/or copper by means of a reducing agent in a suitable nickel salt and/or copper salt solution;

f) electrolytic deposition of tin or a tin alloy in a suitable solution;

g) drying and/or tempering;

h) exerting superficial pressure on the flexible external

electrodes (15, 16) to which solder has already been applied; and

i) applying solder to the external electrodes (15, 16) in protective gas.

2. The method of claim 1, characterized in that the fine cleaning is done with a neutral cleaner, having a pH value of 68, at a temperature preferably of 40 to 60°C.

3. The method of claim 1, characterized in that the pickling is done in a dilute solution of nitric acid with acid additives.

4. The method of claim 1, characterized in that the pickling is done with ultrasonic support, in particular at a frequency of over 40 kHz and at a temperature of 20 to 30°C.

5. The method of claim 1, characterized in that the activation is done in a dilute solution of tin (II) tetrafluoroborate ($Sn(BF_4)_2$) or stannous chloride ($SnCl_2$).

6. The method of claim 1, characterized in that the activation is done at a slightly acidic pH value and/or at a temperature of 30 to 40°C.

7. The method of claim 1, characterized in that the germination is done in a dilute solution of palladium chloride with an addition of halide ions at a pH value of 3 to 4, and in particular at a temperature of 20 to 30°C.

8. The method of claim 1, characterized in that in the currentless deposition, nickel is precipitated out from a nickel

salt solution (such as $NiSO_4$), with phosphinates (such as NaH_2PO_2) as a reducing agent.

9. The method of claim 8, characterized in that the deposition is done at a pH value of 8 to 9 and/or at a temperature of 70 to 95°C.

10. The method of claim 1, characterized in that in the currentless deposition, nickel and copper are precipitated out of a nickel salt solution (such as $NiSO_4$) and a copper salt solution (such as $CuSO_4$) with phosphinates (such as NaH_2PO_2) as the reducing agent and with a hydroxycarboxylic acid as the complexing agent.

11. The method of claim 1, characterized in that in the currentless deposition, copper is precipitated out of a copper salt solution (such as $CuSO_4$) with formaldehyde (CH_2O) as the reducing agent and with a polyaminopolycarboxylic acid as the complexing agent.

12. The method of claim 10, characterized in that the deposition is done at a pH value of 9 to 10 and/or at a temperature of over 60°C.

13. The method of claim 8, characterized in that the deposition is performed over a period of time of 10 to 20 minutes.

14. The method of claim 1, characterized in that in the electrolytic deposition of tin or tin alloys, organic additives, in particular polyaminopolycarboxylic acid, are used as complexing agents.

15. The method of claim 14, characterized in that the deposition is done at a slightly acidic pH value and/or at a temperature of 20 to 40°C.

16. The method of claim 14, characterized in that the deposition is performed over a period of 5 to 30 minutes at a current of 1 to 2 A/dm².

17. The method of claim 1, characterized in that the drying is done in the oil-free nitrogen gas stream.

18. The method of claim 1, characterized in that the tempering is done in a forced air oven at 100 to 200°C over a period of 30 to 60 minutes.

19. The method of claim 1, characterized in that before the exertion of superficial pressure on the external electrodes (15, 16), an ensuing washing off of unneeded flux (no-clean flux) is applied to the suitable outer faces of the multi-layer actuator (10), in particular a 2% adipic acid in ethanol.

20. The method of claim 1, characterized in that for the application of solder, the external electrodes (15, 16) are pressed flat onto the surface mounting metallizing with a pressure of 1 to 5 N/mm².

21. The method of claim 1, characterized in that the application of solder to the external electrodes (13, 14) is done in a continuous furnace at a temperature of 250 to 400°C, and in particular at a feeding speed of 300 to 600 mm/min.

22. The method of claim 1, characterized in that the

application of solder to the external electrodes (13, 14) is done in a vapor-phase soldering system at a temperature of 250 to 290°C.

23. The method of claim 1, characterized in that the activation and/or germination of the desired faces is done by ram application.

24. The method of claim 23, characterized in that the activation and/or germination is done by ram pressure over a period of time of 0.5 to 2 minutes each, in particular at room temperature.

UNITED STATES PATENT AND TRADEMARK OFFICE

Examiner: Group: Attorney Docket # 2075

Applicant(s) : RESCHNAR, W.,ET AL

Serial No. :

Filed :

For : METHOD FOR MOUNTING FLAT EXTERNAL ELECTRODES ON A PIEZOELECTRIC MULTI-LAYER ACTUATOR

INFORMATION DISCLOSURE STATEMENT

March 19, 2002

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

S I R S:

_____ In accordance with the Duty of Disclosure, Applicant(s) submit(s) herewith a copy of a Foreign Search Report in a counterpart application and copies of the reference(s) indicated therein.

___ In the event that the Foreign Search Report is in a foreign language, a translation thereof is herewith submitted.

__X__ Attached hereto is a FORM PTO 1449 listing the references.

_____ Attached hereto is a copy of a reference cited in the specification of the application as filed. The specification itself recites the relevance of these documents.

_____Applicant petitions for consideration of this Information Disclosure Statement since it is being submitted after receipt of an office action and submits herewith the required fee. If this fee is missing or insufficient, then authorization is given to debit the account of the undersigned: 19-4675.

_____ Attached hereto are copies of references cited which may be pertinent to this application. Since the references are in the English language, no statement of relevance is submitted.

_____ Attached hereto is a copy of the Office Action issued in the corresponding German application, together with a translation thereof and copies of the references cited therein. A list of the cited references is also attached.

_____ Attached hereto copies of references cited which may be pertinent to this application. An English translation of the references is also attached.

_____ Attached hereto is a Statement of Relevancy and copies of references cited therein.

__X__ These references were sent to the USPTO by WIPO and are in the file of this application.

Respectfully submitted,

Michael J. Striker
Attorney for Applicant(s)
Reg. No. 27233

INFORMATION DISCLOSURE CITATION

(Use several sheets if necessary)

Docket Number (Optional)	Application Number
2075	10/088620
Applicant(s) RESCHNAR	JC13 Rec'd PCT/PTO 19 MAR 2002
Filing Date	**Group Art Unit**

U.S. PATENT DOCUMENTS

*EXAMINER INITIAL	REF	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE

FOREIGN PATENT DOCUMENTS

	REF	DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS	Translation YES	Translation NO
		34 02 494 A	07/25/85	DE				✓
		197 15 488 C	06/25/98	DE				✓
		196 48 545 A	05/28/98	DE				✓

OTHER DOCUMENTS *(Including Author, Title, Date, Pertinent Pages, Etc.)*

		PATENT ABSTRACTS OF JAPAN VOL. 1995, NO. 09, OCTOBER 31, 1995 & JP 07 162049 A, JUNE 23, 1995.
		PATENT ABSTRACTS OF JAPAN VOL. 1997, NO. 09, SEPTEMBER 30, 1997 & JP 09 135045 A, MAY 20, 1997.

EXAMINER	DATE CONSIDERED

EXAMINER: Initial if citation considered, whether or not citation is in conformance with MPEP Section 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

1/pr

METHOD FOR MOUNTING FLAT EXTERNAL ELECTRODES ON A PIEZOCERAMIC MULTI-LAYER ACTUATOR

PRIOR ART

The invention relates to a method for mounting flat external electrodes on a piezoceramic multi-layer actuator, by which the internal electrodes, extended in alternation outward toward opposed outer sides, are each connected parallel.

One such piezoceramic multi-layer actuator is known for instance from German Patent Disclosure DE 196 48 545 A1. It comprises a sintered stack of thin sheets of piezoceramic, and internal electrodes disposed between the sheets are extended out of the stack toward two opposite sides in alternation and are connected electrically parallel via external electrodes. These external electrodes must be embodied flexibly and must be structured, for instance three-dimensionally. Via partial contact points, they are joined to a foundation metallizing. When an electrical voltage is applied, the stacked multi-layer actuator expands, or upon application of an alternating voltage, it executes expansion and shrinkage motions at the pace of the alternating frequency. Such a multi-layer actuator is used for instance to generate mechanical vibrations or as an actuating device for valves or valve members, for instance for fuel injectors. Because of the mechanical motion of the multi-layer actuator, the foundation metallizing in particular is subjected to a heavy load, and a further factor is that piezoceramic material is intrinsically brittle and has only a slight tensile strength. As a consequence, the maximum allowable tensile stress is often already exceeded in the process of

polarization, so that crack development, especially at the edges, unavoidably occurs and promotes the detachment of a poorly adhering foundation metallizing.

ADVANTAGES OF THE INVENTION

The method of the invention having the characteristics of the main claim advantageously leads to a very well-adhering foundation metallizing and a readily solderable surface mounting metallizing, and the method is in particular also suited to large-scale mass production.

By the provisions recited in the dependent claims, advantageous refinements of and improvements to the method defined by the main claim are possible.

Since the piezoceramic is acid-sensitive, the process baths and process conditions are advantageously selected such that loads occur only in predominantly weakly acidic or alkaline solutions. The special pickling process leads to secure adhesion of the foundation metallizing to the multi-layer actuator.

The surface mounting metallizing of tin or a tin alloy with additives of lead, copper, silver or other alloy components makes good adhesion and secure application of solder to the external electrodes possible. Soldering in a protective gas improves the adhesion to the soldered face. The use of no-clean fluxes makes it possible to dispense with subsequent washing processes.

Especially advantageously, the activation and/or germination is done at the desired faces by means of ram application, preferably over a period of time of 0.5 to 2

minutes each, which can be done at room temperature. As a result, the metallizing is created only on the desired faces, so that postmachining of the other faces can be dispensed with.

DRAWING

A multi-layer actuator with external electrodes with solder applied above a metallizing is shown in longitudinal section in the sole figure of the drawing and will be described in further detail below in terms of the method according to the invention for applying the external metallizing and the external electrodes.

DESCRIPTION OF THE EXEMPLARY EMBODIMENT

In the sole figure of the drawing, a piezoceramic multi-layer actuator is shown schematically. It comprises a sintered stack 10 of thin sheets 11 of piezoceramic, such as lead zirconate titanate. Metal internal electrodes 12, for instance comprising AgPd and applied by screen printing, are attached between the individual sheets 11. These internal electrodes 12 extend in alternation out of the stack 10 as far as its two opposed outsides. There, they are each connected to one another or connected parallel via two external metallizings 13, 14.

The spacing of the internal electrodes 12 from one another is for instance 150 μm, for an electrode thickness of about 5 μm. A multi-layer actuator of this kind comprises several hundred individual electrodes or sheets 11, and this number can be even higher.

Flat, flexible, electrically conductive external

electrodes 15, 16 are soldered to the external metallizings 13, 14 and for the sake of achieving the requisite flexibility can be embodied as mesh screens, nets, spirals, combs, polymers, bronze mesh screens, or the like. This is described in further detail in the prior art cited at the outset.

In the exemplary embodiment, one connection wire 17 in the transverse direction and one connection wire 18 in the longitudinal direction are soldered to the external electrodes, or welded to them, for instance by resistance welding or laser welding. Instead of connection wires, plug contacts could also be applied. This application can be done before or after the application of solder to the external electrodes 15, 16.

When an electrical voltage is applied to the connection wires 17, 18, the stack 10 expands in the direction of the arrow 19; this stroke can for instance be used to actuate a valve or valve member, a fuel injector, or the like. If an alternating voltage is applied, then mechanical vibrations can also be generated in this way.

A process chain for mounting the external metallizings 13, 14 and external electrodes 15, 16 to the stack 10 will now be described.

For the process, the individual stacks 10 or larger bar assemblies that are later cut apart into individual stacks, are already sintered and are retained with ground or lapped outer faces in electroplating frames. The treating of the side faces can be limited to those side faces where the external metallizings 13, 14 are to be mounted.

For the activation process, which is done first, the stacks or bars are first subjected to fine cleaning with a neutral cleaner at a pH value of 6 to 8 and at a temperature of 40 to 60°C for several minutes. This is followed by pickling or roughening of the stacks 10 in dilute solutions of acids or acid mixtures. This operation is done with high-energy ultrasonic support at a frequency of over 40 kHz and at a temperature of 20 to 30°C for several seconds. Next, the actual activation is done in a dilute solution of tin (II) salts, such as $Sn(BF_4)_2$, in the slightly acidic pH range and at a temperature for instance of 30 to 40°C, for several minutes. In the process, tin colloids precipitate out at the outer faces. Finally, germination is done in a dilute solution of palladium chloride in the presence of halide ions, such as $PdCl_2$ + NaCl, at a pH value of 3 to 4 and at a temperature for instance of 20 to 30°C, for several minutes. Instead of palladium, other metals of the platinum group can also be used. The activation can also be done by the application of organic substances. Between each of these treatment steps in the activation, rinsing is done with fully desalinated water.

As the second treatment step, a foundation metallizing of nickel, copper, or a nickel-copper alloy is precipitated out or applied. This treatment step is done in an alkaline solution; the deposition is done in currentless or external-currentless fashion. This can be done by means of three variant methods:

a) Nickel is precipitated out of a nickel salt solution, such as $NiSO_4$, with phosphinates, such as NaH_2PO_2, as reducing agents at a pH value of 8 to 9 and at an elevated temperature, for instance of 70 to 95°C, over a period of time of 10 to 20 minutes.

b) Nickel and copper are precipitated out of a nickel salt solution, such as $NiSO_4$, and a copper salt solution, such as a $CuSO_4$, with phosphinates, such as NaH_2PO_2, as reducing agents and with a hydroxycarboxylic acid as a complexing agent. This is done at a pH value of 9 to 10 and at an elevated temperature, for instance of 80°C, over a period of time of 10 to 30 minutes.

c) Copper is precipitated out of a copper salt solution, such as $CuSO_4$, with formaldehyde (CH_2O) as the reducing agent and with a polyaminopolycarboxylic acid as the complexing agent, at a pH value of 9 to 10 and at an elevated temperature, for instance of 80°C, over a period of time of 10 to 30 minutes.

After the currentless deposition, that is, the application of the foundation metallizing, rinsing is done with fully desalinated water, and immediately an electrolytic surface mounting metallizing with tin or a tin alloy is performed. If an electrolytic surface mounting metallizing directly after the foundation metallizing is not possible, then the process chain can be briefly interrupted by the application of a film of gold approximately 0.1 μm thick. To that end, an externally currentlessly coating gold bath is used, at a neutral to slightly acidic pH value and at elevated temperature.

Because of the acid sensitivity of the piezoceramic used, for the electrolytic deposition of a tin alloy as a solder layer, a solution is used of the kind that for instance is also especially used for lead-containing glasses and ceramics. Because of the severe temperature stress on the multi-layer actuators in later use, for instance in motor vehicles, resistance of the solder to temperatures of up to

230°C must be assured, so that for coating the stacks 10, the solution is adjusted such that a solder with the composition $Sn_{98.5}Pb_{1.5}$, for instance, is obtained. To that end, the tin alloy is deposited as a film onto the stacks 10 or bars by means of a polyaminopolycarboxylic acid as a complexing agent at a slightly acidic pH value and at a temperature for instance of 20 to 40°C. At a current density of 1 to 2 A/dm², solderable film thicknesses are achieved in 15 minutes. Instead of a tin-lead alloy, other tin alloys with copper, bismuth or silver can be used as well. Next, rinsing with fully desalinated water and drying of the stacks in the oil-free nitrogen gas stream are done. As an alternative or additional drying step, the stacks can be tempered in a forced air oven at 100 to 200°C for a period of 30 to 60 minutes.

Finally, as a fourth step, the soldering of the external electrodes 15, 16 to the thus-formed external metallizings 13, 14 is done. First, the stacks 10 or bars are prepared by the application of a so-called no-clean flux, which does not have to be washed off afterward. For instance, a 2% adipic acid in ethanol is suitable. The delivery of the external electrodes 15, 16, to which solder has already been applied, is done via positioning aids, and the electrodes are then pressed flat for instance by means of cup springs, with a pressure for instance of 1 N/mm². The actual soldering is done in a protected gas (such as nitrogen) with a residual oxygen content of less than 10 ppm in a reflow continuous furnace. The temperature profile in the furnace is 250 to 400°C, and the parts are passed through at a feeding speed of 300 to 600 mm/min, in order to achieve a gentle, uniform heating of the stacks 10 to 250°C in 5 to 15 minutes. As an alternative, the solder application can also be done in a vapor-phase soldering system, for instance

at 260°C.

The individual stacks 10 or piezoelectric actuators have vulnerable regions, such as chamfers and side faces, which are foundation-metallized with a chemically reducing metal film (such as nickel) by the described chemical activation and germination in immersion baths, as are the desired contacting sides. For further use, these chamfers and side faces must therefore be cleaned again, for instance by grinding. This often causes the destruction of the multi-layer actuator, especially from the development of short circuits.

In a modification of the method described, for the activation the method described below can therefore be used, which enables a local or selective activation and germination by the ram pressure technique. After the roughening or pickling, the activation is performed with tin (II) tetrafluoroborate by means of a ram application or ram pressure for approximately 1 minute at room temperature. The activation is therefore done only in those regions that were covered in an outline corresponding to the shape of the ram. The ensuing germination can also be done via ram pressure for approximately 1 minute at room temperature, so that the thin nickel film is formed in a desired way only in the shape of the ram, while the other faces remain bare. This applies to the ensuing surface mounting metallizing as well.

Claims

1. A method for mounting flat external electrodes (15, 16) on a piezoceramic multi-layer actuator (10), by which the internal electrodes (12), extended in alternation outward toward opposed outer sides, are each connected parallel, characterized by the treatment of at least the outer faces that are to be provided with the external electrodes (15, 16) by the following method steps:

a) fine cleaning with a neutral cleaning agent;

b) pickling in a dilute acid solution;

c) activation in a dilute solution of an activation agent;

d) germination in a dilute solution of palladium chloride with an addition of halide ions or of another halide of a metal of the platinum group with palladium or another metal of the platinum group;

e) currentless deposition of nickel and/or copper by means of a reducing agent in a suitable nickel salt and/or copper salt solution;

f) electrolytic deposition of tin or a tin alloy in a suitable solution;

g) drying and/or tempering;

h) exerting superficial pressure on the flexible external electrodes (15, 16) to which solder has already been

applied; and

i) applying solder to the external electrodes (15, 16) in protective gas.

2. The method of claim 1, characterized in that the fine cleaning is done with a neutral cleaner, having a pH value of 68, at a temperature preferably of 40 to 60°C.

3. The method of claim 1 or 2, characterized in that the pickling is done in a dilute solution of nitric acid with acid additives.

4. The method of one of the foregoing claims, characterized in that the pickling is done with ultrasonic support, in particular at a frequency of over 40 kHz and at a temperature of 20 to 30°C.

5. The method of one of the foregoing claims, characterized in that the activation is done in a dilute solution of tin (II) tetrafluoroborate ($Sn(BF_4)_2$) or stannous chloride ($SnCl_2$).

6. The method of one of the foregoing claims, characterized in that the activation is done at a slightly acidic pH value and/or at a temperature of 30 to 40°C.

7. The method of one of the foregoing claims, characterized in that the germination is done in a dilute solution of palladium chloride with an addition of halide ions at a pH value of 3 to 4, and in particular at a temperature of 20 to 30°C.

8. The method of one of the foregoing claims,

characterized in that in the currentless deposition, nickel is precipitated out from a nickel salt solution (such as $NiSO_4$), with phosphinates (such as NaH_2PO_2) as a reducing agent.

9. The method of claim 8, characterized in that the deposition is done at a pH value of 8 to 9 and/or at a temperature of 70 to 95°C.

10. The method of one of claims 1-7, characterized in that in the currentless deposition, nickel and copper are precipitated out of a nickel salt solution (such as $NiSO_4$) and a copper salt solution (such as $CuSO_4$) with phosphinates (such as NaH_2PO_2) as the reducing agent and with a hydroxycarboxylic acid as the complexing agent.

11. The method of one of claims 1-7, characterized in that in the currentless deposition, copper is precipitated out of a copper salt solution (such as $CuSO_4$) with formaldehyde (CH_2O) as the reducing agent and with a polyaminopolycarboxylic acid as the complexing agent.

12. The method of claim 10 or 11, characterized in that the deposition is done at a pH value of 9 to 10 and/or at a temperature of over 60°C.

13. The method of one of claims 8-11, characterized in that the deposition is performed over a period of time of 10 to 20 minutes.

14. The method of one of the foregoing claims, characterized in that in the electrolytic deposition of tin or tin alloys, organic additives, in particular polyaminopolycarboxylic acid, are used as complexing agents.

15. The method of claim 14, characterized in that the deposition is done at a slightly acidic pH value and/or at a temperature of 20 to 40°C.

16. The method of claim 14 or 15, characterized in that the deposition is performed over a period of 5 to 30 minutes at a current of 1 to 2 A/dm².

17. The method of one of the foregoing claims, characterized in that the drying is done in the oil-free nitrogen gas stream.

18. The method of one of the foregoing claims, characterized in that the tempering is done in a forced air oven at 100 to 200°C over a period of 30 to 60 minutes.

19. The method of one of the foregoing claims, characterized in that before the exertion of superficial pressure on the external electrodes (15, 16), an ensuing washing off of unneeded flux (no-clean flux) is applied to the suitable outer faces of the multi-layer actuator (10), in particular a 2% adipic acid in ethanol.

20. The method of one of the foregoing claims, characterized in that for the application of solder, the external electrodes (15, 16) are pressed flat onto the surface mounting metallizing with a pressure of 1 to 5 N/mm².

21. The method of one of the foregoing claims, characterized in that the application of solder to the external electrodes (13, 14) is done in a continuous furnace at a temperature of 250 to 400°C, and in particular at a feeding speed of 300 to 600 mm/min.

22. The method of one of claims 1-20, characterized in that the application of solder to the external electrodes (13, 14) is done in a vapor-phase soldering system at a temperature of 250 to 290°C.

23. The method of one of the foregoing claims, characterized in that the activation and/or germination of the desired faces is done by ram application.

24. The method of claim 23, characterized in that the activation and/or germination is done by ram pressure over a period of time of 0.5 to 2 minutes each, in particular at room temperature.

Abstract

A method for mounting flat external electrodes (15, 16) on a piezoceramic multi-layer actuator is proposed, in which by means of the external electrodes (15, 16), the internal electrodes (12) extended in alternation to opposite outsides, are each connected parallel. The outer faces to be provided with the external electrodes (15, 16) are treated by the following method steps:

a) fine cleaning with a neutral cleaning agent;

b) pickling in a dilute acid solution;

c) activation in a dilute solution of an activation agent;

d) germination in a dilute solution of palladium chloride with an addition of halide ions or of another halide of a metal of the platinum group with palladium or another metal of the platinum group;

e) currentless deposition of nickel and/or copper by means of a reducing agent in a suitable nickel salt and/or copper salt solution;

f) electrolytic deposition of tin or a tin alloy in a suitable solution;

g) drying and/or tempering;

h) exerting superficial pressure on the flexible external electrodes (15, 16) to which solder has already been

applied; and

i) applying solder to the external electrodes (15, 16) in protective gas.

By this method, a very firmly adhering foundation metallizing and a readily solderable surface mounting metallizing are attained, and the method is suited to mass production.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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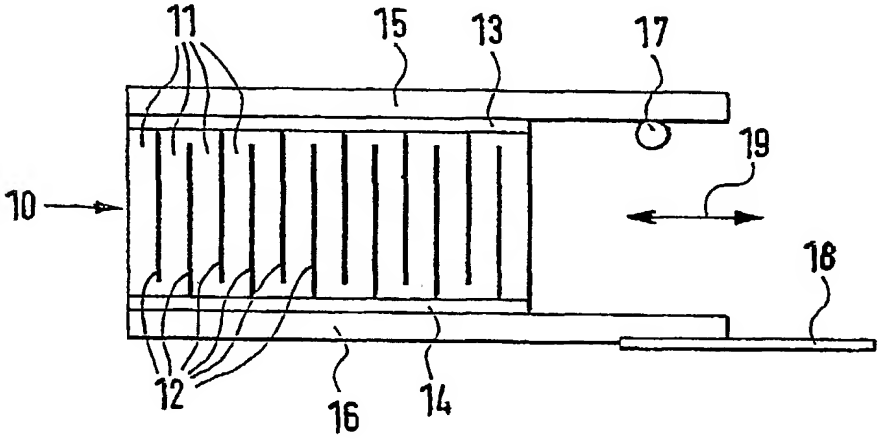
(81) Bestimmungsstaaten *(national)*: CN, JP, KR, US.

[Fortsetzung auf der nächsten Seite]

(54) Title: METHOD FOR APPLYING FLAT OUTER ELECTRODES TO A PIEZOCERAMIC MULTI-LAYER ACTUATOR

(54) Bezeichnung: VERFAHREN ZUR ANBRINGUNG VON FLÄCHIGEN AUSSENELEKTRODEN AUF EINEM PIEZOKERAMISCHEN VIELSCHICHTAKTOR



(57) Abstract: The invention relates to a method for applying flat outer electrodes (15, 16) to a piezoceramic multi-layer actuator. The inner electrodes (12) which are alternately guided towards and through opposite outsides are switched in parallel by means of the outer electrodes (15, 16). The outer surfaces that are to be provided with the outer electrodes (15, 16) are pre-treated in a wet-chemical manner. The outer metal coatings (13, 14) are produced by currentlessly depositing nickel and/or copper and galvanically depositing tin or a tin alloy. The outer electrodes (15, 16) are finally soldered on under a protective gas. A very solidly adhering base metal coating and a well solderable finishing metal coating are obtained by the inventive method which can be used for mass production.

(57) Zusammenfassung: Es wird ein Verfahren zur Anbringung von flächigen Außenlektroden (15, 16) auf einem piezokeramischen Vielschichtaktor vorgeschlagenen, wobei durch die Außenelektroden (15, 16) die wechselseitig nach entgegengesetzten Außenseiten hin herausgeführten Innenelektroden (12) jeweils parallelgeschaltet werden. Die mit den Außenelekroden (15, 16) zu versehenden Außenflächen werden zunächst naßchemisch vorbehandelt. Die Herstellung der Außenmetallisierung (13, 14) erfolgt durch stromloses Abscheiden von Nickel und/oder

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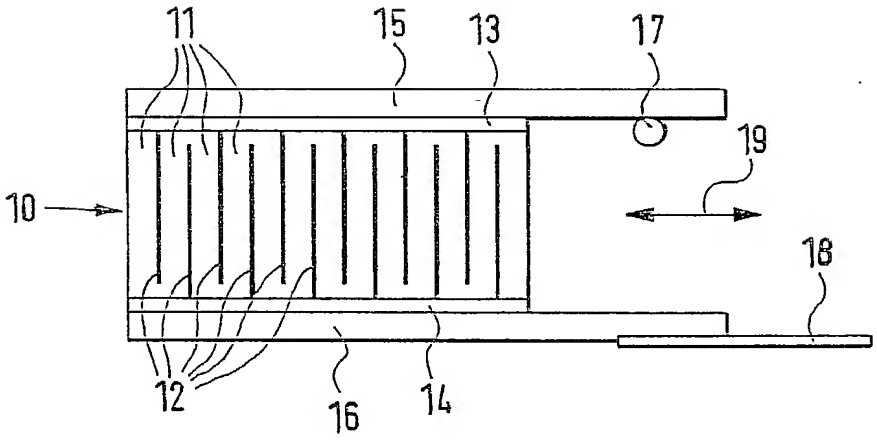
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DECLARATION AND POWER OF ATTORNEY FOR NATIONAL STAGE OF PCT PATENT APPLICATION

As a below-named inventor, I hereby declare that:

Wilfried RESCHNAR
Lothar HENNEKEN
Bertram SUGG
Juergen HACKENBERG

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **METHOD FOR MOUNTING FLAT EXTERNAL ELECTRODES ON A PIEZOCERAMIC MULTI-LAYER ACTUATOR** the specification of which was filed as PCT International Application number PCT/DE 00/03135 filed on September 9, 2000.

I hereby state that I believe the named inventor or inventors in this Declaration to be the original and first inventor or inventors of the subject matter which is claimed and for which a patent is sought.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365 (b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior foreign application(s):			Priority claimed:	
199 45 267.9	GERMANY	SEPTEMBER 21, 1999	X	
(Number)	(Country)	(Date filed)	Yes	No
(Number)	(Country)	(Date filed)	Yes	No

As a named inventor, I hereby appoint the following attorney to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with

the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statement may jeopardize the validity of the application or any patent issued thereon.

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Full Name of Sixth Inventor:	Citizenship:	
Signature:	Date:	Residence and Full Postal Address:
Full Name of Seventh Inventor:	Citizenship:	
Signature:	Date:	Residence and Full Postal Address:
Full Name of Eighth Inventor:	Citizenship:	

March 19, 2002

DECLARATION

The undersigned, Jan McLin Clayberg, having an office at 5316 Little Falls Road, Arlington, VA 22207-1522, hereby states that she is well acquainted with both the English and German languages and that the attached is a true translation to the best of her knowledge and ability of international patent application PCT/DE 00/03135 of RESCHNAR, W., et al., entitled "METHOD FOR MOUNTING FLAT EXTERNAL ELECTRODES ON A PIEZOCERAMIC MULTI-LAYER ACTUATOR".

The undersigned further declares that the above statement is true; and further, that this statement was made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or document or any patent resulting therefrom.

Jan McLin Clayberg